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NONADIABATIC THEORY OF
ELECTRON-HYDROGEN SCATTERING

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SUMMARY

A rigorous theory of the s-wave elastic scattering of elec-
trons from hydrogen is presented. The Schrödinger equation is
reduced to an infinite set of coupled two-dimensional partial dif-
ferential equations. A zeroth order scattering problem is defined
by neglecting the coupling terms of the first equation. An exact
relation is derived between the phase shift of this zeroth order
problem and the true phase shift. The difference between these
is given by a rapidly convergent series whose terms correspond
adiabatically to multipole distortions of the hydrogen by the in-
coming electron. Recognition of the physical significance of the
zeroth order problem is considered basic to the understanding of
the scattering problem. The exchange approximation for s-wave
scattering is shown to be a variational approximation of the
zeroth order problem. A perturbation theory is introduced to
calculate the higher order corrections. The dipole correction has
an increasingly important quantitative effect in the limit of zero
energy. The effect of the long range part of this correction on
the scattering length can be expressed by a formula in terms of
inverse powers of a long range parameter R. Phase shifts are
calculated for both singlet and triplet scattering, including up to
quadrupole terms. The convergence is such that this number of
terms should yield better than four place accuracy. Uncertainties
in the calculated values decrease the accuracy to approximately
three significant figures.

CONTENTS

LIST OF SYMBOLS

E — Total energy. $E = -1 + k^2$. The term -1 is the energy of H atom and k^2 is the energy of the impinging electron.

$P_l \left(\cos \theta_{12} \right)$ — Legendre polynomials of order l of $\cos \theta_{12}$.

r_1 — The distance of electron 1 from the nucleus.

r_2 — The distance of electron 2 from the nucleus.

$R_{ns}(r_2)$ — The s-eigenstates of hydrogen. In particular $R_{1s}(r_2) = 2r_2 e^{-r_2}$ is the ground state.

δ — Exact s-wave phase shift.

δ_0 — Phase shift of the zeroth order problem. That is,

$$\lim_{r_1 \to \infty} \Phi_0^{(0)} \left(r_1, r_2 \right) = \sin \left(kr_1 + \delta_0 \right) R_{1s}(r_2)$$

$\Delta^l \delta_0^{(j)}$ — The various order corrections to δ_0. That is, $\delta = \delta_0 + \sum_{l=1}^{\infty} \sum_{j=1}^{l} \Delta^l \delta_0^{(j)}$.

θ_{12} — The angle between the lines connecting electrons 1 and 2 to the nucleus.

$\Phi_l(r_1 r_2)$ — Functions in the basic expansion of

$$\Psi \left(r_1, r_2, \theta_{12} \right) = \frac{1}{r_1 r_2} \sum_{l=0}^{\infty} (2l + 1)^{\frac{1}{2}} \Phi_l \left(r_1, r_2 \right) P_l \left(\cos \theta_{12} \right) .$$

$\Phi_0 \left(r_1, r_2 \right)$ — Only non-vanishing of the Φ_l's in the limit $r_1 \to \infty$. That is,

$$\lim_{r_1 \to \infty} \Psi \left(r_1, r_2, \theta_{12} \right) = \lim_{r_1 \to \infty} \Phi_0 \left(r_1, r_2 \right)$$

$$= \sin \left(kr_1 + \delta \right) R_{1s}(r_2)$$

$\Phi_0^{(0)}(r_1, r_2)$ — Exact solution of the simplified s-wave problem (zeroth order problem).

$\Psi \left(r_1 r_2 \theta_{12} \right)$ — Solution of the s-wave scattering problem.

NONADIABATIC THEORY OF ELECTRON-HYDROGEN SCATTERING [*][†]

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INTRODUCTION

The elastic scattering of electrons from atomic hydrogen is the most fundamental three-body scattering problem of quantum mechanics. Nevertheless, the process of theoretical understanding has been slow and is still not complete.

Specifically, the lack of a real quantitative understanding of this problem—as compared with its counterpart, the ground state of helium problem—can be traced to two causes. The first was the lack of a minimum principle which guarantees not only that a certain quantity is variational in character, but, more important, that it is greater than (or less than) the exact quantity to be evaluated. The lack of a minimum principle has recently been overcome by Rosenberg, Spruch, and O'Malley, who have derived minimum principles for the scattering length (Reference 1) and who are attempting to generalize the procedure to include phase shifts as well (Reference 2).

The second aspect of scattering problems which has slowed the process of quantitative understanding is simply the fact that the scattering parameters are more sensitive functions of the wave function than, say, the ground state energy. This sensitivity may be illustrated in the case of the singlet scattering of electrons by hydrogen, where there is known to be a singlet bound state of the H^- ion with a binding energy of 14.460 electron volts (ev). The electron affinity ϵ is defined as the difference between this energy and that of a hydrogen atom and a free electron. Clearly ϵ is the quantity of physical significance, for only when it is negative is the H^- bound. Being a small difference between two large numbers, ϵ is obviously sensitive to deviations in one of the large numbers. An approximation which undershoots the total energy by 6 percent predicts no binding. The fact that the H^- wave function corresponds to a barely bound system means that it must be related to the low energy (e-H) scattering wave function. This relationship is expressed by the

approximate formula (Reference 3)

$$\sqrt{|\epsilon|} = \frac{1}{a} + \frac{1}{2} r_0 |\epsilon| \quad ,$$

which shows that the effective range parameters a and r_0 are also sensitive functions of the wave function.[1]

The sensitivity of the scattering parameters (the phase shifts) to the wave function manifests itself in another way. Suppose, in considering a scattering problem, that an attempt is made to replace the interaction of the incident particle with the (many-body) target by an equivalent one-body potential. In the bound state problem, it is known that the Hartree or Hartree-Fock method leads to just such an equivalent potential. In the case of scattering of a particle from a compound system consisting of particles *different* from the incoming particle, Mittleman and Watson (Reference 6) have developed formal expressions for just such a potential, and Mittleman (Reference 7) has modified the approach to apply to the scattering of electrons from hydrogen. However, the equivalent potential is effectively a series expansion in which the derivation of successive terms is a major calculational task, particularly for the in-close behavior of the potential, and in which the physical meaning of successive terms becomes increasingly obscure. In addition, the potentials become quite nonlocal in character and appear to present considerable difficulties for numerical solution (M. Mittleman, private communication).

The difficulty of evaluating a potential that is valid over all space is symptomatic of the essentially non-two-body character of the scattering problem. The main idea of the method that we shall present here is that the correct zeroth order problem is a three-body problem. However, given the basic three-body problem, there are a variety of ways of handling it. *Thereafter,* the corrections are separable in the first approximation. The method we shall present is an extension of the method of Luke, Meyerott, and Clendenin (Reference 8).[2] The chief formula is Equation 13, which relates the zeroth-order phase shift δ_0 with the exact phase shift δ. The main property of the terms on the right-hand side of Equation 13 is that they constitute a rapidly convergent series. They also have a natural physical interpretation as long-range polarization effects. The quantitative importance of the lower of these terms is basically an expression of the increased importance of polarization in (most) scattering problems as opposed to (most) ground state energy problems. The polarization terms constitute the part of the wave function from which the extra sensitivity of the scattering parameters stems. Yet the main contribution of these functions comes from the (adiabatic) region where the functions are separable. The nonadiabatic method, however, projects equations for these functions over all space;

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[1] The effective range formalism for the (e-H) problem has been effectively exploited by Ohmura, Hara, and Yamaouchi (Reference 4) and by Ohmura and Ohmura (Reference 5).

[2] The author is indebted to Mr. John W. Cooper for having brought this paper to his attention.

various devices can be employed to get reasonable estimates of the contributions of these functions from the nonadiabatic region even without solving the associated partial differential equations. This will be the subject of the succeeding sections. We shall conclude with the evaluation of fairly accurate electron-hydrogen phase shifts, and, more important, with a reliable estimate of the error.

DECOMPOSITION OF THE S-WAVE EQUATION

The s-wave scattering of electrons from hydrogen is described by the Schrödinger equation of zero total angular momentum for two electrons in the field of a singly charged nucleus (assumed infinitely heavy). Such an equation can be reduced to a three-dimensional partial differential equation which can be written (Reference 9)

$$\left[-\frac{1}{r_1}\frac{\partial^2 r_1}{\partial r_1^2} - \frac{\partial^2 r_2}{r_2 \partial r_2^2} - \left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\frac{1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}\sin\theta_{12}\frac{\partial}{\partial\theta_{12}} \right.$$

$$\left. -\frac{2}{r_1} - \frac{2}{r_2} + \frac{2}{r_{12}} - E \right] \psi\left(r_1, r_2, \theta_{12}\right) = 0 . \tag{1}$$

where energy units are rydbergs (1 ryd = 13.6 ev) and length units are Bohr radii. The fact that the s-wave equation can be reduced to a single three-dimensional equation is the main mathematical reason that it is susceptible to a highly quantitative treatment.

Because the Legendre polynomials $P_l(\cos\theta)$ are eigenfunctions of the angular dependent operator in the above equation, that is,

$$\frac{1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}\sin\theta_{12}\frac{\partial}{\partial\theta_{12}}P_l\left(\cos\theta_{12}\right) = -l(l+1) P_l\left(\cos\theta_{12}\right) , \tag{2}$$

the wave function can be expanded into

$$\psi\left(r_1, r_2, \theta_{12}\right) = \frac{1}{r_1 r_2}\sum_{l=0}^{\infty} \sqrt{2l+1}\, \Phi_l\left(r_1 r_2\right) P_l\left(\cos\theta_{12}\right) . \tag{3}$$

Substitution into Equation 1 then gives an infinite set of coupled equations

$$\left[\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} - l(l+1)\left(r_1^{-2} + r_2^{-2}\right) + E + \frac{2}{r_1} + \frac{2}{r_2} - M_{ll} \right] \Phi_l\left(r_1 r_2\right) = \sum_m{}' M_{lm}\Phi_m\left(r_1 r_2\right) \tag{4}$$

4

where in the region $r_1 > r_2$,

$$M_{lm} = \sqrt{(2l+1)(2m+1)} \sum_{n=0}^{l+m} \frac{r_2^n}{r_1^{n+1}} \int_0^\pi P_l(\cos\theta) P_m(\cos\theta) P_n(\cos\theta) \sin\theta \, d\theta \ . \tag{5}$$

Under exchange $(r_1 \rightleftarrows r_2)$ the three coordinates of the s-wave problem transform according to $r_1 \rightleftarrows r_2$ and $\theta_{12} \to \pi + \theta_{12}$. Thus, the singlet and triplet Ψ functions must have the property $\Psi(r_1, r_2, \theta_{12}) = \pm\Psi(r_2, r_1, \theta_{12})$ respectively. In terms of the expansion function Φ_l this implies (as a necessary and sufficient condition) that

$$\Phi_l(r_1 r_2) = \pm\Phi_l(r_2 r_1) \ .$$

The symmetry of the bracketed operator in Equation 1 further implies that the problem can be solved completely in the region $r_1 \geq r_2$ by imposing the additional boundary conditions

$$\left.\Phi_l(r_1 r_2)\right|_{r_1 = r_2} = 0 \qquad \text{triplet} \left.\begin{array}{c} \\ \\ \\ \end{array}\right\}, \tag{6}$$

$$\left.\frac{\partial}{\partial n}\Phi_l(r_1 r_2)\right|_{r_1 = r_2} = 0 \qquad \text{singlet}$$

where $\partial/\partial n$ means the normal derivative. Because of the $r_1 r_2$ factor in Equation 3, we have in both cases

$$\Phi_l(r_1 0) = 0 \ . \tag{7}$$

We are restricting ourselves to the description of scattering below the threshhold for inelastic scattering; thus, we must also have

$$\lim_{r_1 \to \infty} \Phi_0(r_1 r_2) = \sin(kr_1 + \delta) R_{1s}(r_2)$$

$$\tag{8}$$

$$\lim_{r_1 \to \infty} \Phi_l(r_1 r_2) = 0, \ l > 0 \ .$$

Here k is the momentum of the scattered electron and is related to the energy by

$$E = -1 + k^2 \ .$$

and $R_{1s}(r)$ is r times the (normalized) ground state radial function of the hydrogen.

The s-wave phase shifts δ are then completely specified by the coupled set of Equations 4 subject to the boundary conditions of Equations 6 through 8.

Clearly such a set of equations must be solved in some approximate manner. What we would like to give in the sequel is a basis for such a method of successive approximations. The virtue of the method of approximation is that there is obvious physical signicance in each stage and that both physical and mathematical reasons for the rapid convergence of the series can be readily established. A central role in this scheme is the zeroth order approximation, which we shall now consider.

THE ZEROTH ORDER APPROXIMATION
AND THE MULTIPOLE EXPANSION

Since

$$M_{0m} = \frac{2}{\sqrt{2m+1}} \frac{r_2^m}{r_1^{m+1}} , \tag{9}$$

the equation for $\Phi_0\left(r_1, r_2\right)$ can be written explicitly as

$$\left(\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + E + \frac{2}{r_2}\right) \Phi_0\left(r_1 r_2\right) = \sum_{m=1}^{\infty} \frac{2}{\sqrt{2m+1}} \frac{r_2^m}{r_1^{m+1}} \Phi_m . \tag{10}$$

It is natural to attempt to approximate this equation by neglecting the right-hand side. Consider

$$\left(\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + E + \frac{2}{r_2}\right) \Phi_0^{(0)}\left(r_1 r_2\right) = 0 \tag{11}$$

subject to the boundary conditions of Equations 6 and 7 for $\Phi_0^{(0)}$, and with the asymptotic form

$$\lim_{r_1 \to \infty} \Phi_0^{(0)}\left(r_1 r_2\right) = \sin\left(kr_1 + \delta_0\right) R_{1s}\left(r_2\right) . \tag{12}$$

It is important to realize that, although the right-hand side of Equation 12 is an exact solution of Equation 11, δ_0 is *not* arbitrary.
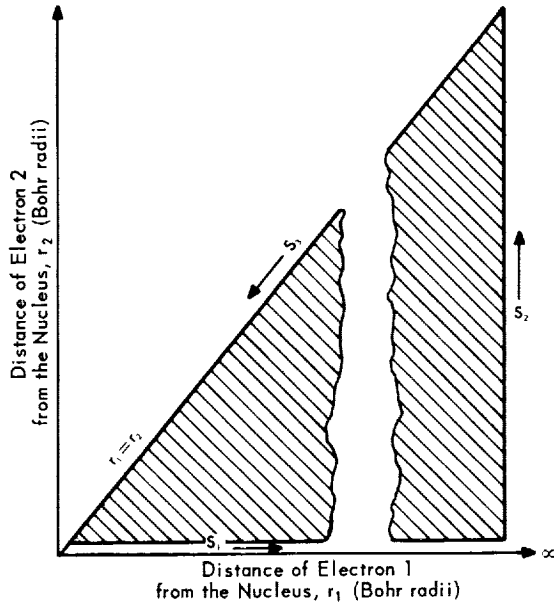
Figure 1 — The $r_1 > r_2$ triangle to which the whole mathematical problem is restricted.

In the language of partial differential equations, Equation 11 is an elliptic equation with Dirchlet boundary conditions along all sides for the triplet case and with Neumann conditions along s_3 in the singlet case (Figure 1). The boundary condition along s_2 is

$$\Phi_0^{(0)}(\infty, r_2) = C R_{1s}(r_2) ,$$

where C is an arbitrary constant corresponding to the arbitrariness in normalization of $\Phi_0^{(0)}$. For a given C, δ_0 is clearly independent of C. The uniqueness of the solution for a given C then guarantees that δ_0 is unique.

A relation between δ_0 and δ can be established by multiplying Equation 11 by Φ_0 and Equation 10 by $\Phi_0^{(0)}$, subtracting and integrating over the half plane $r_2 \leq r_1$; this gives

$$\int_0^\infty \int_0^{r_1} \left(\Phi_0 \Delta_{12} \Phi_0^{(0)} - \Phi_0^{(0)} \Delta_{12} \Phi_0 \right) dr_1 dr_2 = -\sum_{m=1}^\infty \int_0^\infty \int_0^{r_1} \Phi_0^{(0)} M_{0m} \Phi_m dr_1 dr_2 .$$

The operator

$$\Delta_{12} \equiv \frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2}$$

is the two-dimensional Laplacian, and using Green's theorem, we can write the left-hand side of Equation 12 as

$$\int_0^\infty \int_0^{r_1} \left(\Phi_0 \Delta_{12} \Phi_0^{(0)} - \Phi_0^{(0)} \Delta_{12} \Phi_0 \right) dr_1 dr_2 = \int_s \left(\Phi_0 \frac{\partial}{\partial n} \Phi_0^{(0)} - \Phi_0^{(0)} \frac{\partial}{\partial n} \Phi_0 \right) ds .$$

The boundary s goes around the region $r_1 > r_2$ and is thus the triangle indicated in Figure 1. The line integral along s_1 is zero by virtue of Equation 7 and its counterpart for $\Phi_0^{(0)}$. The integral along s_3 is zero by Equation 6 so that we are left with only the integral

along s_2. Here $\partial/\partial n = \partial/\partial r_1$, and using the asymptotic forms of Φ_0 and $\Phi_0^{(0)}$, Equations 7 and 12, and the assumption that R_{1s} is normalized, we arrive at our main formula

$$\sin(\delta - \delta_0) = -\frac{1}{k} \sum_{m=1}^{\infty} \frac{2}{\sqrt{2m+1}} \int_0^\infty dr_1 \int_0^{r_1} \Phi_0^{(0)} \frac{r_2^m}{r_1^{m+1}} \Phi_m \, dr_2 \quad . \tag{13}$$

Equation 11 is the zeroth order problem and δ_0 the zeroth order phase shift. It must be emphasized that in spite of the separability of Equation 11 as a partial differential equation, the problem is nonseparable by virtue of the nonseparable boundary condition for $\Phi_0^{(0)}$ (see equation 18 below). The physical meaning of the equation is clear. Electron 1 comes in seeing no charge at all while the orbital electron (electron 2) sees the whole nuclear charge. When electron 1 gets inside the orbit of electron 2, it sees the whole nuclear charge and becomes the orbital electron while electron 2 goes off as the scattered particle seeing no charge. This, of course, is nothing but the shielding approximation as it applies to a scattering problem. Yet, because the position of electron 1 is correlated with the position of electron 2, which itself is variable, this is distinctly a three-body problem. It is the thesis of this report that this rudimentary three-body problem lies at the core of this, the s-wave elastic scattering problem, and that attempts at further reduction either are equivalent to mathematical reformulations of the problem or they bring in dubious approximations.

It is not difficult to show that the exchange approximation (Reference 10), which uses an ansatz Ψ_{EA} not depending on the angle θ_{12}, that is,

$$r_1 r_2 \Psi_{EA} = u(r_1)' R_{1s}(r_2) \pm u(r_2) R_{1s}(r_1) \quad ,$$

for the s-wave function, is in fact a variational solution of only that part of the original Schrödinger equation corresponding to Equation 11. For if we consider the matrix element of the complete interaction, $+\frac{2}{r_1} + \frac{2}{r_2} - \frac{2}{r_{12}}$, with any (symmetric or antisymmetric) function of the form $f(r_1, r_2)$ then[3]

$$\iint f^* (r_1, r_2)\left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{2}{r_{12}}\right) f(r_1, r_2) d^3 r_1 d^3 r_2 \, \alpha \int_0^\infty \int_0^\infty \left| r_1 r_2 f(r_1, r_2) \right|^2 \frac{2}{r_<} dr_1 dr_2$$

$$= 2 \int_0^\infty dr_1 \int_0^{r_1} \left| r_1 r_2 f(r_1, r_2) \right|^2 \frac{2}{r_2} dr_2 \, ,$$

[3]Geltman (Reference 11) has computed variational phase shifts, using wave functions, which for s-waves are functions of r_1 and r_2 only. According to our analysis, his phase shifts are approximations of the zeroth order δ_0 only. McEachran and Fraser (Reference 12) and Smith (Reference 13) have used the close-coupling extension of the exchange approximation including various numbers of excited s-states in their wave functions. These too can only approximate δ_0.

8

where we have used the (anti) symmetry of $f\left(r_1, r_2\right)$. (Note that other terms of the Schrödinger equation will also yield matrix elements in this region multiplied by a factor of 2.) We shall see in the next section that the exchange approximation yields phase shifts practically identical[4] to δ_0. Therefore, it is an excellent approximation of $\Phi_0^{(0)}$, yet from Equation 13 we see that it neglects the higher order corrections associated with the function Φ_i.

One more remark is in order concerning the zeroth order problem and δ_0 in particular: there are no long-range polarization forces associated with the zeroth order problem, so that the boundary conditions associated with $\Phi_0^{(0)}$, aside from its s-wave sinusoidal behavior at infinity, are very much like a bound-state problem. This is quite different from the phase shift of the whole problem in which there are long-range polarization forces, which are, however, manifested in Φ_l $(l > 0)$. A practical consequence of this is that δ_0 considered as a function of r_1 quickly assumes its asymptotic form as is typical for a particle scattered from a short-range potential. In fact, the Hartree-Fock exchange approximation potential is an exponentially decaying one. Thus, in contrast to δ, which only slowly assumes its asymptotic form, δ_0 can truly be regarded as unvarying for large r_1. (This consideration is relevant in the derivation of Equation 52.)

The physical meaning of the functions Φ_l can be gleaned from the adiabatic region (defined as the region $r_1 \gg r_2$ and $r_1 \gg 1$). In this region, only the function Φ_0 fails to vanish and only the first term $\left(-2r_1^{-1}\right)$ of M_{ll} in Equation 4 need be considered. Thus, these equations reduce to

$$\left(\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} - \frac{l(l+1)}{r_2^2} + \frac{2}{r_2} - 1 + k^2\right)\Phi_l = \frac{2r_2^l}{\sqrt{2l+1}} \frac{\sin\left(kr_1 + \delta\right)}{r_1^{l+1}} R_{1s}\left(r_2\right) . \qquad (14)$$

A solution of this equation, neglecting the operation $\partial^2/\partial r_1^2$ on $r_1^{-(l+1)}$ (which we assume is justified in this region), is

$$\Phi_l \approx \frac{-2}{\sqrt{2l+1}} \frac{\sin\left(kr_1 + \delta\right)}{r_1^{l+1}} e^{-r_2}\left(\frac{r_2^{l+2}}{l+1} + \frac{r_2^{l+1}}{l}\right). \qquad (15)$$

These functions represent multipole distortions of the hydrogen atom caused by an electron at some distance from the atom (Reference 14 and 15).

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[4]Although ψ_{EA} is gotten from a separable picture of the interaction, the requirement that it have the correct symmetry makes it, in fact, nonseparable. The combination of the symmetry and nonseparability, the fact that the zeroth order problem contains no long-range polarization which is also true of ψ_{EA}, and the variational nature of the equations for $u(r)$ all combine to make ψ_{EA} an excellent approximation of $\Phi_0^{(0)}$. Reference 14 stresses the fact that correct treatment of the symmetry goes a long way toward including the nonseparability (nonadiabaticity). This is the fortunate circumstance which has allowed investigators to calculate not unreasonable estimates of the low energy scattering of *electrons* from atoms, starting the significant work of Morse and Allis (Reference 10).

Having obtained the adiabatic form of Φ_l, we can now qualitatively establish the convergence of Equation 13. The configuration space of each double integral can be divided into roughly four regions, schematically indicated in Figure 2. In region D, the adiabatic region, the explicit forms of $\Phi_0^{(0)}$ and Φ_l can be used to see that the contributions from that region go down rapidly as a function of l. In region C where $r_2 \approx r_1$ and both are large, the contribution is very small in all cases. This is because $\Phi_0^{(0)}$ and the Φ_l decay exponentially there, roughly as $\exp\left[-(r_1 + r_2)\sqrt{\frac{1}{2}\ E}\right]$.

(Note that $E < -\frac{1}{4}$ for all the energies being considered.) In region A where both r_1 and r_2 are small, the Φ_l's$(l > 0)$ are nec-

Figure 2 — The regions of configuration space which give different magnitude contributions to the multiple integrals.

essarily small by virtue of the centrifugal barrier $-l(l + 1)\left(r_1^{-2} + r_2^{-2}\right)$ which pushes the wave functions out from that region.[5] For intermediate values of r_1 and r_2 (region B) there will be an important quantitative contribution whose convergence as a function of l stems from the gradual disappearance of the region B itself as region A merges into regions C and D.

As a function of increasing energy, the multipole terms on the right-hand side of Equation 13 have a decreasingly important effect on the cross section. Nevertheless the quantitative contribution of these terms becomes more difficult to calculate. This is because at the lowest energies the proportionate contribution from region D is sizeable, yet the function is known there. For higher energies the proportionate contribution from region D becomes quite small.

SOLUTION OF THE ZEROTH ORDER PROBLEM

It has already been emphasized that Equation 11, together with the boundary conditions

$$\Phi_0^{(0)}(r_1 0) = 0 , \tag{16}$$

$$\lim_{r_1 \to \infty} \Phi_0^{(0)}(r_1 r_2) = \sin\left(kr_1 + \delta_0\right) R_{1s}(r_2) , \tag{17}$$

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[5]The presence of the centrifugal terms for $l > 0$ is the main reason why the associated Φ_l can be considered separable in zeroth order, whereas $\Phi_0^{(0)}$ cannot.
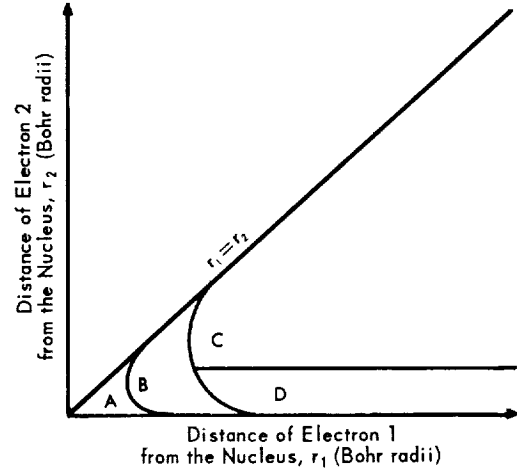
10

and

$$\Phi_0^{(0)}\left(r_1 r_2\right)\Big|_{r_1 = r_2} = 0 \qquad \text{triplet}$$

$$\frac{\partial}{\partial n}\Phi_0^{(0)}\Big|_{r_1 = r_2} = 0 \qquad \text{singlet}$$

$$\tag{18}$$

presents a highly nonseparable problem. Nevertheless, Equation 11 itself is separable, and the separable solutions can readily be written down. We shall expand the exact solution $\Phi_0^{(0)}$ in terms of the totality of all such separable solutions which can possibly enter the expansion:

$$\Phi_0^{(0)} = \sin\left(kr_1 + \delta_0\right)R_{1s}\left(r_2\right) + \left(\sum_n + \int d\rho\right)C_n e^{-\kappa_n r_1} R_{ns}\left(r_2\right) . \tag{19}$$

The sum plus integral means, as usual, that the continuum s states of hydrogen in addition to the discrete states must be included. For the discrete states

$$\kappa_n = \sqrt{1 - n^{-2} - k^2} , \tag{20}$$

and for the continuum states

$$\kappa_\rho = \sqrt{1 + \rho^2 - k^2} . \tag{21}$$

Since each term of Equation 18 is separately a solution of Equation 11, the only thing which prevents any expansion from being an exact solution is its deviation from the boundary condition, Equation 18. (Note that Equations 16 and 17 are automatically satisfied.) We therefore determine δ_0 and the C_n's by the variational condition

$$\delta \int_0^\infty \left| \Phi_0^{(0)}\left(r_1 = r_2\right)\right|^2 dr_1 = 0 \qquad \text{triplet,}$$

$$\delta \int_0^\infty \left| \frac{\partial}{\partial n}\Phi_0^{(0)}\right|^2_{r_1 = r_2} dr_1 = 0 \qquad \text{singlet.}$$

$$\tag{22}$$

Substituting Equation 19 into the triplet integral in Equation 22 gives

$$I_T \equiv \int_0^\infty \left| \Phi_0^{(0)} \left(r_1 = r_2 \right) \right|^2 \, dr_1$$

(23)

$$= \int_0^\infty \sin^2 \left(kr + \delta_0 \right) R_{1s}^2(r) \, dr + 2 \sum_{j=1}^N C_j Y_j + \sum_{j=1}^N C_j^2 (ME)_{jj} + 2 \sum_{i>j=1}^N C_i C_j (ME)_{ij}$$

where

$$(ME)_{ij} = \int_0^\infty e^{-\left(\kappa_i + \kappa_j \right) r} R_{is}(r) R_{js}(r) \, dr \quad , \tag{24}$$

and

$$Y_i = \int_0^\infty \sin \left(kr + \delta_0 \right) e^{-\kappa_i r} R_{1s}(r) R_{is}(r) \, dr \equiv \cos \delta \mathfrak{N}_{si} + \sin \delta \mathfrak{N}_{ci} \quad . \tag{25}$$

The variation implicit in Equation 22 now becomes

$$\left. \begin{array}{ll} \dfrac{\partial I_T}{\partial C_i} = 0 \, , & i = 1,2,3 \ldots, N. \, , \\[4mm] \dfrac{\partial I_T}{\partial \delta_0} = 0 \, . & \end{array} \right\} \tag{26}$$

The first N equations are

$$Y_j + \sum_{j=1}^N C_i (ME)_{ji} \equiv 0 \, , \qquad j = 1,2,3,\ldots, N \, .$$

These may be solved for the C_i to give

$$C_i = \frac{-1}{\det} \left[D_s^{(i)} \cos \delta_0 + D_c^{(i)} \sin \delta_0 \right] \, , \tag{27}$$

12

where det is the determinant of the matrix elements:

$$
\det \equiv \det \begin{pmatrix} (ME)_{11} & (ME)_{12} & \cdots & (ME)_{1N} \\ (ME)_{21} & (ME)_{22} & \cdots & (ME)_{2N} \\ \vdots & \vdots & & \vdots \\ (ME)_{N1} & (ME)_{N2} & \cdots & (ME)_{NN} \end{pmatrix}
$$

$D_s^{(i)}$ and $D_c^{(i)}$ are determinants obtained by replacing the ith column of the above matrix by the columns $\left(\mathfrak{N}_{s1}, \mathfrak{N}_{s2}, \ldots, \mathfrak{N}_{sn}\right)$ and $\left(\mathfrak{N}_{c1}, \mathfrak{N}_{c2}, \ldots, \mathfrak{N}_{cn}\right)$, respectively.

The variation with respect to δ_0 gives

$$
\frac{\partial I_T}{\partial \delta_0} = \int_0^\infty \sin\left[2\left(kr + \delta_0\right)\right] R_{1s}^2 \, dr + 2\sum_{i=1}^N C_i \int_0^\infty \cos\left(kr + \delta_0\right) R_{is} \, dr = 0 . \tag{29}
$$

Using Equation 27 for the C_i's, and noting that

$$
\sum_{i=1}^N D_s^{(i)} \mathfrak{N}_{ci} = \sum_{i=1}^N D_c^{(i)} \mathfrak{N}_{si} , \tag{30}
$$

we can rewrite Equation 29 in the form

$$
0 = \cos\left(2\delta_0\right) N_{2s} + \sin\left(2\delta_0\right) N_{2c} - \frac{2}{\det} \sin\delta_0 \cos\delta_0 \sum_{i=1}^N \left(D_c^{(i)} \mathfrak{N}_{ci} - D_s^{(i)} \mathfrak{N}_{si}\right)
$$

$$
- \frac{2}{\det}\left(\cos^2\delta_0 - \sin^2\delta_0\right) \sum_{i=1}^N D_s^{(i)} \mathfrak{N}_{ci} ,
$$

where

$$
\left. \begin{aligned} N_{2s} &= \int_0^\infty \sin\left(2kr\right) R_{1s}^2 \, dr , \\[2ex] N_{2c} &= \int_0^\infty \cos\left(2kr\right) R_{1s}^2 \, dr . \end{aligned} \right\} \tag{31}
$$

We may readily solve for $\tan 2\delta_0$ since

$$\tan 2\delta_0 = - \frac{N_{2s} - \frac{2}{\det} \sum_{i=1}^{N} D_s^{(i)} \pi_{ci}}{N_{2c} + \frac{1}{\det} \sum_{i=1}^{N} \left(D_s^{(i)} \pi_{si} - D_c^{(i)} \pi_{ci} \right)} \; . \tag{32}$$

A completely analogous procedure may be used to solve for $\tan 2\delta_0$ in the singlet case. We obtain

$$\tan 2\delta_0 = - \frac{\frac{1}{2} A_s - k B_c - \frac{2}{\det s} \sum_{i=1}^{N} \nu_i D_\mu^{(i)}}{\frac{1}{2} A_c + k B_s + \frac{1}{\det s} \sum_{i=1}^{N} \left(\mu_i D_\mu^{(i)} - \nu_i D_\nu^{(i)} \right)} \; , \tag{33}$$

and

$$C_i = \frac{D_\mu^{(i)} \cos \delta_0 + D_\nu^{(i)} \sin \delta_0}{\det s} \; , \tag{34}$$

where

$$\det s = \text{determinant} \left\| \int_0^\infty \Psi_i \Psi_j dr \right\| \; , \tag{35}$$

in which

$$\Psi_i = \left[\left(-\frac{\partial}{\partial r_1} + \frac{\partial}{\partial r_2} \right) e^{-\kappa_i r_1} R_{is}(r_2) \right]_{r_1 = r_2} \; . \tag{36}$$

Let

$$\Psi_0 = \left[\left(-\frac{\partial}{\partial r_1} + \frac{\partial}{\partial r_2} \right) \sin(k r_1 + \delta_0) R_{1s}(r_2) \right]_{r_1 = r_2} \; ; \tag{37}$$

then μ_i and ν_i are quantities independent of δ_0 defined by

$$-\int_0^\infty \Psi_0 \Psi_i dr = \mu_i \cos \delta_0 + \nu_i \sin \delta_0 \; .$$

Also,

$$A_s \equiv 8 \int_0^\infty \sin(2kr)\left[1 - 2r + \left(1 - k^2\right)r^2\right]e^{-2r}\,dr \quad ,$$

$$A_c \equiv 8 \int_0^\infty \cos(2kr)\left[1 - 2r - \left(1 - k^2\right)r^2\right]e^{-2r}\,dr \quad ,$$

$$B_s \equiv 8 \int_0^\infty \sin(2kr)r(1 - r)e^{-2r}\,dr \quad ,$$

$$B_c \equiv 8 \int_0^\infty \cos(2kr)r(1 - r)e^{-2r}\,dr \quad .$$

The determinants $D_\mu^{(i)}$ and $D_\nu^{(i)}$ are obtained by replacing the ith column of dets by the column vectors $(\mu_1, \mu_2, \ldots, \mu_N)$ and $(\nu_1, \nu_2, \ldots, \nu_N)$, respectively.

It is worth pointing out the converse nature of this technique of solution as distinguished from those usually employed. In most cases the exact solution is approximated in terms of functions which are not solutions of the equation, but which do satisfy all the boundary conditions. In close-coupling, for example, the basis functions are solutions of part but not all of the equations. The method presented here uses functions which are complete solutions of the equation, but which do not satisfy all the boundary conditions. In the present method, the smallness of the deviation from the boundary condition is a very reliable index of the quality of the solution (provided that this difference is small enough).

The method of performing actual calculations is then as follows: A selection of N discrete and/or continuum terms is made (we are necessarily limited to a discrete sampling of the continuum states), and all the matrix elements and integrals in Equations 32 and 33 are evaluated. (Integrals involving discrete states are trivial. Pertinent formulas for continuum states are included in Appendix A.) This, then, can be used to evaluate $\tan 2\delta_0$ from Equations 32 and 33. Then $2\delta_0$ modulo π is determined from $\tan 2\delta_0$. The correct quadrant of $2\delta_0$ is determined by noting which value actually minimizes I_T (or I_s). This determines δ_0 modulo π. (At this point it is known for (e-H) scattering that $\delta_0 \to \pi$ from below as $k \to 0$, so that in fact no ambiguity remains.)[6]

Numerical calculations were coded for the IBM 7090 computer at the Goddard Space Flight Center. The program allowed an arbitrary number of terms (limited only by the capacity of the machine) to be included. In practice, however, the number of terms was

---

[6]This example is discussed in connection with an absolute definition of phase shift in Reference 16. The same definition has also been adopted by Rosenburg and Spruch (Reference 2).

restricted to less than 10 by an initially unexpected circumstance: As the number of terms was increased, det, dets, and the related determinants approached zero so rapidly that all the significant figures contained in the evaluation of the matrix elements were quickly lost. Therefore, the number of terms had to be restricted so that at least some significant figures remained. Actually, not too many significant figures need be known because any set of C_i's and δ_0 can be considered an approximate expansion of $\Phi_0^{(0)}$ and its quality can be measured by the smallness of I_T or I_S.

A sample of the pertinent results for the triplet and singlet calculations have been collected in Tables 1 and 2. The last column contains the exchange approximate results which, as was proved earlier, are a variational approximate solution of the zeroth order problem. It is clear that the approximation is in excellent agreement with the exact result (see footnote 3 page 7). It can be seen from Tables 1 and 2 that the triplet phase shifts are leass variable and therefore can be more accurately determined than the singlet phase shifts. This disparity is indicative of the greater accuracy that is obtainable for the triplet results in all parts of the calculation. Note that I_T and I_S are positive definite. These quantities were calculated from Equation 23 and its singlet counterpart, by using numbers evaluated by the machine from the analytic formulas for $(ME)_{ij}$, etc. The fact that some of the entries are negative is due to the cancellation of all significant figures. Thus, in those cases, a zero deviation from the boundary condition to within the accuracy of the machine has been obtained. (The accuracy of the machine is estimated to be from five to seven places.) Because of the loss of significant figures, the smallness of I_T and I_S in Tables 1 and 2 cannot be taken as an unambiguous measure of the reliability of δ_0 for the various expansions of $\Phi_0^{(0)}$. Nevertheless, somewhat better accuracy in δ_0 can be obtained than can currently be achieved for the higher order corrections.

EVALUATION OF THE MULTIPOLE CORRECTIONS

Although the right-hand side of Equation 13 converges rapidly, there still remains an assumption which must be true if the effectiveness of this method is not to be an illusion: The coupling of the lower to the higher Φ_l in Equation 4 must *not* be such that omitting the higher in the equation for the lower Φ_l substantially changes the latter's contribution to $\sin\left(\delta - \delta_0\right)$. Actually, our assertion concerning the importance of the adiabatic contribution guarantees this situation for small k. For in the adiabatic region, only Φ_0 does not vanish, and this coupling is taken into account in Equations 14 and 15. So, if this region gives the major contribution to the integrals on the right-hand side of Equation 13, then we can be sure that the neglect of the higher order couplings cannot materially change the value of the integrals.

We shall introduce a perturbation theory which is based on this assumption. The perturbation theory does not do away with the partial differential equations. (In fact, the essence of this method is that partial differential equations are the most natural way to

Table 1

Triplet Results for $\Phi_0^{(0)}$ and δ_0

The first line of each entry refers to the terms used in the expansion of $\Phi_0^{(0)}$. The second line is δ_0 in radians. The third line is the diagonal sum I_T.

k				Exchange
0.01	$2,3,I_0$ 3.11820 -0.165×10^{-7}	$2,4,I_0$ 3.11823 -0.149×10^{-7}	$2,4,I_0,I_5,I_{10},I_{20}$ 3.11821 -0.424×10^{-8}	3.118
0.05	$2,3,I_0$ 3.0247 0.160×10^{-6}	$2,4,I_0$ 3.0255 0.168×10^{-5}	$2,4,I_0,I_5,I_{10},I_{20}$ 3.0257 0.244×10^{-5}	3.024
0.1	$2,3,I_0$ 2.9084 0.283×10^{-6}	$2,4,I_0$ 2.9097 0.465×10^{-5}	$2,4,I_0,I_5,I_{10},I_{20}$ 2.9102 0.699×10^{-5}	2.907
0.2	$2,3,I_0$ 2.6806 0.153×10^{-5}	$2,4,I_0$ 2.6807 0.173×10^{-5}	$2,4,I_0,I_5,I_{10},I_{20}$ 2.6809 0.283×10^{-5}	2.679
0.3	$2,3,I_0$ 2.4634 0.722×10^{-5}	$2,4,I_0$ 2.4629 0.433×10^{-5}	$2,4,I_0,I_5,I_{10},I_{20}$ 2.4632 0.549×10^{-5}	2.461
0.4	$2,3,I_0$ 2.2582 0.113×10^{-5}	$2,4,I_0,I_5,I_{10},I_{20}$ 2.2588 0.201×10^{-5}	$2,4,I_0,I_3,I_5,I_7,I_{10},I_{20}$ 2.2589 0.169×10^{-5}	2.257
0.5	$2,4,I_0$ 2.0715 0.477×10^{-5}	$2,4,I_0,I_5,I_{10},I_{20}$ 2.0716 0.398×10^{-5}	$2,4,I_0,I_3,I_5,I_7,I_{10},I_{20}$ 2.0721 0.365×10^{-5}	2.070
0.75	$2,4,I_0$ 1.6914 0.355×10^{-3}	$2,3,4,I_0,I_1,I_2,I_3,I_7$ 1.6830 0.497×10^{-4}	$2,3,4,I_0,I_1,I_1,I_2,I_3$ 1.6830 0.474×10^{-4}	1.679
0.8	$2,3,4,I_0,I_1,I_2,I_3$ 1.61664 -0.117×10^{-4}	$2,3,4,I_0,I_1,I_2I_3,I_7$ 1.61665 -0.123×10^{-4}	$2,4,I_0,I_3,I_5,I_7,I_{10},I_{20}$ 1.6220 0.18×10^{-2}	1.614

Table 2

Singlet Results for $\Phi_0^{(0)}$ and δ_0

The first line(s) of each entry refers to the terms used in the expansion of $\Phi_0^{(0)}$. The second line is δ_0 in radians. The third line is the diagonal sum I_s.

k					Exchange
0.01	$3,4$ 3.0638 -0.373×10^{-8}	$4,I_0$ 3.0637 -0.186×10^{-7}	$3,I_0,I_3$ 3.0636 -0.198×10^{-7}	$3,4,I_3,I_4$ 3.0643 0.242×10^{-7}	3.0606
0.05	$4,I_0$ 2.7595 -0.238×10^{-6}	$4,I_0,I_4$ 2.7596 -0.263×10^{-6}	$3,I_0$ 2.7591 0.157×10^{-6}	$3,I_0,I_3$ 2.7593 0.149×10^{-6}	2.746
0.1	$5,I_0,I_5$ 2.4207 0.774×10^{-6}	$4,I_0,I_2,I_3,I_4$ 2.4174 0.783×10^{-6}	$4,I_0,I_3$ 2.4182 0.918×10^{-6}	$4,I_0,I_4,I_8,I_{12},I_{16}$ 2.4177 0.934×10^{-6}	2.396
0.2	$2,3,I_1,I_2,I_3,I_4$ 1.8949 0.777×10^{-5}	$2,5,I_1,I_2,I_3,I_4$ 1.8968 0.142×10^{-4}	$2,I_0,I_1,I_2,I_3,I_4$ 1.8947 0.193×10^{-4}	$3,4,I_1,I_2,I_3$ 1.8960 0.253×10^{-4}	1.870
0.3	$2,5,I_1,I_2,I_3,I_4$ 1.5350 0.183×10^{-4}	$2,I_0,I_1,I_2,I_3,I_4,I_5$ 1.5321 0.291×10^{-4}	$2,4,I_1,I_2,I_3,I_4$ 1.5348 0.129×10^{-4}	$2,3,I_0,I_6$ 1.5245 0.295×10^{-4}	1.508
0.4	$2,4,I_1,I_2,I_3$ 1.2694 0.489×10^{-6}	$2,5,I_1,I_2,I_3,I_4$ 1.2691 0.150×10^{-5}	$2,I_0,I_1,I_2,I_3,I_4$ 1.2685 0.693×10^{-5}	$2,3,I_2,I_3$ 1.2697 0.134×10^{-4}	1.239
0.5	$3,4,I_1,I_2$ 1.0667 0.926×10^{-5}	$3,5,I_1,I_2,I_3,I_4$ 1.0652 0.353×10^{-4}	$2,I_0,I_1,I_2,I_3,I_4,I_5$ 1.0647 0.375×10^{-4}	$2,I_0,I_2,I_4,I_6,I_8$ 1.0656 0.459×10^{-4}	1.031
0.75	$2,3,4,I_{.75},I_{1.5},$ $I_{2.25},I_3,I_{3.75},I_{4.5}$ 0.7556 0.517×10^{-5}	$2,3,I_0,I_{.5},I_1$ $I_{1.5},I_2$ 0.7564 0.117×10^{-4}	$2,3,4,I_{.5},I_1,I_{1.5}$ $I_2,I_{2.5}$ 0.7535 0.109×10^{-4}	$2,I_0,I_{.5},I_1,I_{1.5}$ $I_2,I_{2.5}$ 0.7566 0.131×10^{-4}	0.694
0.8	$2,4,5,I_{.75},I_{1.5},$ $I_{2.25}$ 0.7289 0.170×10^{-4}	$2,3,I_0,I_{.5},I_1,I_{1.5}$ $I_2,I_{2.5}$ 0.7268 0.175×10^{-4}	$2,3,4,I_{.75},I_{1.5},I_{2.25}$ $I_3,I_{3.75},I_{4.5}$ 0.7261 0.212×10^{-4}	$2,3,4,I_{.5},I_1,I_{1.5}$ $I_2,I_{2.5}$ 0.7273 0.228×10^{-4}	0.651

include nonadiabaticity in both $\Phi_0^{(0)}$ and the higher Φ_l.) Rather, it allows the equations to be solved in a sequential manner. It also allows the construction of "sum rules" which, to a more limited accuracy, allow for evaluation of the multipole terms without the need to solve the associated partial differential equations[7] beyond what is done in Equation 15.

A measure of the adiabaticity of a region of configuration space is the quantity r_2^n/r_1^{n+1}. We shall assign to this quantity an order of magnitude $\lambda^{n/2}$ in accord with the fact that the larger n is, the smaller this quantity is in a given region of configuration space. The functions Φ_l are expanded according to

$$\Phi_l = \sum_{j=0}^{\infty} \lambda^{j+\frac{l}{2}} \Phi_l^{(j)} \ .$$

This embodies the notion that the higher Φ_l's get successively smaller in the adiabatic region and their behavior away from the adiabatic region can be expanded in a series about their behavior in the adiabatic region.[8] Using these expansions and the order of magnitude associated with adiabatic factor r_2^n/r_1^{n+1}, we can reduce Equation 4 to a set of equations characterized by increasing powers of $\lambda^{\frac{1}{2}}$. To order $\lambda^{\frac{3}{2}}$ we obtain:

$$\lambda^0: \quad \left(\Delta_{12} + 2r^{-2} + E\right) \Phi_0^{(0)} = 0 \ , \tag{38}$$

$$\lambda^{\frac{1}{2}}: \quad \left[\Delta_{12} - 2\left(r_1^{-2} + r_2^{-2}\right) + 2r_2^{-1} + E\right] \Phi_1^{(0)} = 2(3)^{-\frac{1}{2}} r_2 r_1^{-2} \Phi_0^{(0)} \ , \tag{39}$$

$$\lambda: \quad \left(\Delta_{12} + 2r_2^{-1} + E\right) \Phi_0^{(1)} = 2(3)^{-\frac{1}{2}} r_2 r_1^{-2} \Phi_1^{(0)} \ , \tag{40}$$

$$\left[\Delta_{12} - 6\left(r_1^{-2} + r_2^{-2}\right) + 2r_2^{-1} + E\right] \Phi_2^{(0)} = 2(5)^{-\frac{1}{2}} r_2^2 r_1^{-3} \Phi_0^{(0)} \ , \tag{41}$$

$$\lambda^{\frac{3}{2}}: \quad \left[\Delta_{12} - 2\left(r_1^{-2} + r_2^{-2}\right) + 2r_2^{-1} + E\right] \Phi_1^{(1)} - \frac{4}{5} r_2^2 r_1^{-3} \Phi_1^{(0)} = \tag{42}$$

$$2(3)^{-\frac{1}{2}} r_2 r_1^{-2} \Phi_0^{(1)} + 4(15)^{-\frac{1}{2}} r_2 r^{-2} \Phi_2^{(0)} \ .$$

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[7] In conjunction with Sullivan and Cahill of NASA, we have been able to solve the second order partial differential equations numerically. This will be the basis of very precise calculations.

[8] This expansion would not be very good in the region $r_1 \approx r_2$ if we were interested in the values of Φ_l. A re-expression of our basic idea, however, would be to say that we need not know the wave function equally well in all space. Rather, we must know $\Phi_0^{(0)}$ in all space, in accord with that function's essentially three-body nature. For $l > 0$, Φ_l may be known less well because only integrals over Φ_l contribute to the phase shift; and in those integrals the contribution of the region $r_1 \approx r_2$ has only limited importance *for the electron-hydrogen problem*.

The multipole series (Equation 13) becomes an expansion in integral powers of λ:

$$\sin\left(\delta-\delta_0\right) = -\frac{1}{k}\sum_{\nu=1}^{\infty}\lambda^\nu \sum_{\substack{m+\mu=\nu \\ m\geq 1,\,\mu\geq 0}} \frac{2}{\sqrt{2m+1}} \int_0^\infty \int_0^{r_1} \Phi_0^{(0)}\,\frac{r_2^m}{r_1^{m+1}}\,\Phi_m^{(\mu)}\,dr_1 dr_2 \ , \tag{43}$$

where λ^ν is the expected order of magnitude of the correction to δ_0. The first order correction is

$$\Delta\delta_0 \equiv -\frac{1}{k}\,\frac{2}{\sqrt{3}} \int_0^\infty \int_0^{r_1} \Phi_0^{(0)}\,\frac{r_2}{r_1^2}\,\Phi_1^{(0)}\,dr_1 dr_2 \ . \tag{44}$$

This is the dipole contribution with the exact Φ_1 replaced by $\Phi_1^{(0)}$. The second order contribution consists of two terms $\Delta^2\delta_0^{(1)} + \Delta^2\delta_0^{(2)}$, where

$$\Delta^2\delta_0^{(2)} \equiv \frac{-2}{k\sqrt{5}} \int_0^\infty \int_0^{r_1} \Phi_0^{(0)}\,\frac{r_2^2}{r_1^3}\,\Phi_2^{(0)}\,dr_1 dr_2 \ , \tag{45}$$

$$\Delta^2\delta_0^{(1)} \equiv \frac{-2}{k\sqrt{3}} \int_0^\infty \int_0^{r_1} \Phi_0^{(0)}\,\frac{r_2}{r_1^2}\,\Phi_1^{(1)}\,dr_1 dr_2 \ . \tag{46}$$

Of course, $\Delta^2\delta_0^{(2)}$ is the perturbation theoretic approximation of the quadrupole term, but $\Delta^2\delta_0^{(1)}$ is a dipole term. It represents the first order correction on Φ_1 due to the coupling to Φ_0 in the nonadiabatic region. The fact that this term enters in the order λ^2 means that this contribution is expected to an order of magnitude less than $\Delta\delta_0$. It will be seen that the calculated results are excellently consistent with this assumption.

The calculation itself was carried out to order λ^2. This requires, in principle, the solution of Equations 38 through 42. Actually, the fact that the asymptotic form of the functions is known allows us to achieve reasonably accurate phase shifts without further solving these equations. The adiabatic forms of the functions $\Phi_l^{(0)}$ are:

$$\Phi_l^{(0)} \approx \frac{-2r_1^{-(l+1)}}{\sqrt{2l+1}}\sin\left(kr_1 + \delta_0\right)e^{-r_2}\left(\frac{r_2^{l+2}}{l+1} + \frac{r_2^{l+1}}{l}\right) . \tag{47}$$

The asymptotic form of $\Phi_1^{(1)}$ in the adiabatic region is

$$\Phi_1^{(1)} \approx -\frac{2}{\sqrt{3}}\left(\Delta\delta_0\right)\frac{\cos\left(kr_1 + \delta_0\right)}{r_1^2}e^{-r_2}\left(\frac{r_2^3}{2} + r_2^2\right) . \tag{48}$$

If a large portion of the various integrals comes from the adiabatic region, it is clear that Equations 47 and 48 alone will give a not unreasonable estimate of their size. More about these functions is known, namely their boundary conditions along $r_1 = r_2$. In the triplet case the function vanishes, and a factor which will do this for $\Phi_l^{(0)}$ can easily be appended. We have used

$$\Phi_l^{(0)} = \frac{-2 \sin\left(kr_1 - \delta_0\right)}{\sqrt{2l+1} \; r_1^{l+1}} e^{-r_2}\left(\frac{r_2^{l+2}}{l+1} + \frac{r_1^{l+1}}{l}\right)\left[1 - l^{-D_l\left(r_1 - r_2\right)}\right] . \tag{49}$$

The positive constant D_l can be fairly unambiguously determined as will be shown below. In the singlet case there is no simple factor which will make the normal derivative of $\Phi_l^{(0)}$ zero along $r_1 = r_2$. We have used

$$\Phi_l^{(0)} = \frac{-2}{\sqrt{2l+1}} \frac{\sin\left(kr_1 + \delta_0\right)}{\left(r_1^{l+1} + D_l\right)}\left(e^{-r_2}\right)\left(\frac{r_2^{l+2}}{l+1} + \frac{r_2^{l+1}}{l}\right) , \tag{50}$$

the cutoff factor having been inserted in such a way as to give $\Phi_l^{(0)}$ the expected behavior $\Phi_l^{(0)} \rightarrow r_1^{l+1}$ in the limit $r_2 \rightarrow r_1 \rightarrow 0$.

The determination of D_l was accomplished in the following way. By essentially the same method as that used to derive Equation 13, "sum rules" of the form

$$\int_0^\infty \int_0^{r_1} \Phi_0^{(0)}\left[-l(l+1)\left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\right]\Phi_l^{(0)} \, dr_1 dr_2 = \frac{2}{\sqrt{2l+1}} \int_0^\infty \int_0^{r_1} \frac{r_2^l}{r_1^{l+1}}\left(\Phi_0^{(0)}\right)^2 dr_1 \, dr_2 \tag{51}$$

can be derived from Equation 38 and the equations like Equations 39 and 41.

The functions $\Phi_0^{(0)}$ are known from the zeroth order calculation; thus the right-hand sides of Equation 51 could be evaluated. The forms of Equations 49 and 50 were used in conjunction with $\Phi_0^{(0)}$ to evaluate the left-hand side as a function of D_l . The adopted values of D_l were those which gave equality. (Some of the results are shown in Figures 3 and 4.) These values of D_l were then used to evaluate the terms on the right-hand side of Equation 43, in particular $\Delta\delta_0$, $\Delta^2\delta_0^{(2)}$, and $\Delta\delta_0^{(1)}$.

The types of cutoffs we have used do not introduce any bending of nodal lines in the $r_1 > r_2$ triangle. Such behavior is reasonable for the lowest energies. At high energies the bending would be expected to become significant; thus, the errors intrinsic to the calculation will probably go up.

Exp. of $\phi_0^{(0)}$ 2, 4, I_0, I_5, I_{10}, I_{20}

$$\frac{2}{\sqrt{3}} \iint \left(\phi_0^{(0)}\right)^2 \frac{r_2}{r_1^2}$$

$$\iint \phi_0^{(0)} \left[-2\left(\frac{1}{r_1^2} + \frac{1}{r_1^2}\right) \right] \phi_1^{(0)}$$

Exp. of $\phi_0^{(0)}$ 2, 3, 10

Cutoff Parameter D_1 (Bohr radii^{-1})

Value of the Integrals (appropriate units)
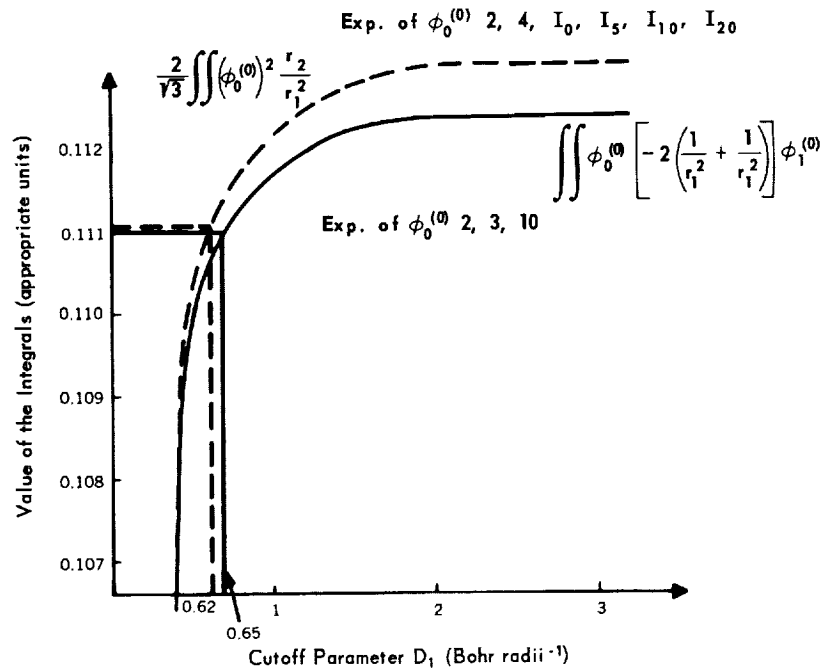
Figure 3 — Triplet dipole sum rule for $k = 0.1$ and two different expansions of $\Phi_0^{(0)}$. The values of $\Delta\delta_0$ using the two expansions of $\Phi_0^{(0)}$ and the respective values of D_1 in $\Phi_1^{(0)}$ are 0.0303 and 0.0304.

$$\iint \phi_0^{(0)} \left[-6\left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right) \right] \phi_2^{(0)}$$

$$\frac{2}{\sqrt{5}} \iint \left(\phi_0^{(0)}\right)^2 \frac{r_2^2}{r_1^3}$$

Value of the Integrals (appropriate units)

Cutoff Parameter D_2 (Bohr radii^2)
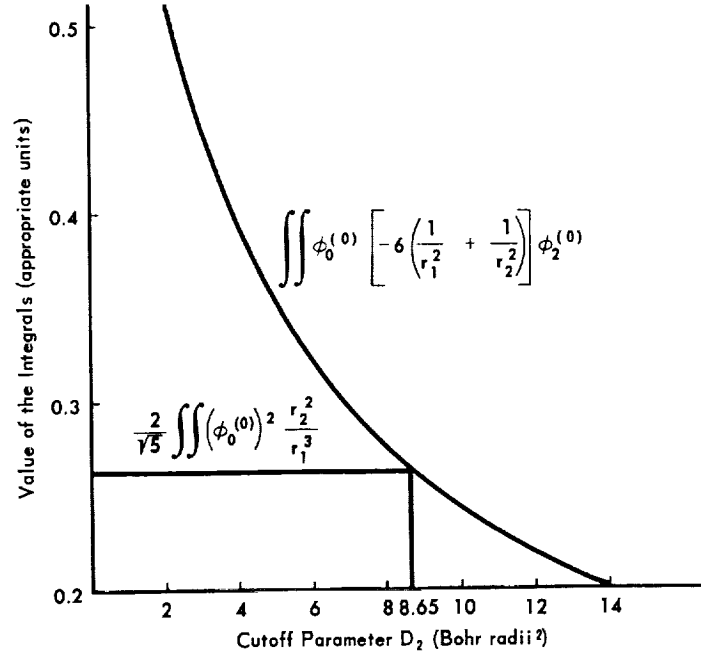
Figure 4 — Single quadrupole sum rule for $k = 0.5$. Different expansions of $\Phi_0^{(0)}$ give curves which are indistinguishable on this scale. Value of $\Delta^2\delta_0^{(2)}$ for this case is 0.0232.

In calculating $\Delta^2\delta_0{}^{(1)}$ we have used the same type of cutoffs for $\Phi_1{}^{(1)}$ as for $\Phi_1{}^{(0)}$. It is possible to derive "sum rules" which tend to indicate that the value of D to be used should be somewhere between the dipole value D_1 and the quadrupole D_2. Nevertheless, the contribution of this function from the nonadiabatic region is expected to be greater than its contribution from the adiabatic region. In addition, judging from Equation 42, we expect its behavior in the nonadiabatic region to be much more complicated there. Thus, our evaluation of $\Delta^2\delta_0{}^{(1)}$ should be considered somewhere between a calculation and an estimate.

In practice, all double integrals were done numerically. Thus, it was necessary to stop the integration over r_1 at a finite point $r_1 = R$. It is important, however, to take into account the contribution of the integral for $r_1 > R$ in the limit of zero energy. Fortunately, this can be done analytically. The analysis for the effect of this long-range behavior on the scattering length has already been given.[9] A somewhat more careful derivation yields

$$a = a(R) - \alpha\left(\frac{1}{R} - \frac{a + a_0}{2R^2}\right), \tag{52}$$

where a is the exact scattering length, a_0 is the scattering length of the zeroth order problem, and $a(R)$ is the scattering length associated with the part of the wave function within radial distances of R of the nucleus. Equation 52 is another result of long-range induced polarization indicative of the basic difference between a bound-state and a scattering problem. For a value of $R = 25$, a bound-state wave function has essentially assumed its asymptotic form, whereas the portion of the wave function beyond $R = 25$ contributes (negatively) almost 10 percent to the triplet scattering length.[9] Equation 52 is valid for any method in which only the part of the configuration space for r_1, $r_2 < R$ is included.

The contributions from large r die off rapidly as k is increased, to the extent that they are negligible for our accuracy by $k = 0.1$. Tables 3 and 4 summarize the singlet and triplet calculated results. The δ_0's are a somewhat visual mean of the values in Tables 1 and 2. The convergence of the higher terms is evident. The final δ's contain in parentheses the estimated uncertainty of the last figure(s). The convergence is such that all higher multipole contributions should be smaller than this uncertainty. The error is again an estimate of those due to δ_0 and the higher multipoles. (The quantities in parentheses in the other columns are not deviations from the electron-hydrogen phase shifts, but rather from the exact phase shifts of well defined but different mathematical problems.) The greatest absolute error of the higher multipoles is contained in $\Delta\delta_0$ (although it contains the smallest proportional error). In the triplet case, the errors have been estimated at from about 5 percent to 25 percent, for increasing k. In the

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[9]This analysis is contained in Reference 17 together with the result of our triplet scattering length calculation. At that time the significant reduction from the RSO bound (Reference 1) was completely unexpected.

Table 3

Resumé of Calculation for Triplet δ

k	δ_0	$\Delta\delta_0$	$\Delta^2\delta_0^{(1)}$	$\Delta^2\delta_0^{(2)}$	δ	δ(polarized orbital)
0[†]	2.338 (3)				1.76 (3)	1.7[‡] (1)
0.01	3.11821(2)	0.00504	0.000295	0.000153	3.1237(4)	3.125[‡]
0.05	3.025 (1)	0.0193	0.0013	0.0008	3.046 (5)	3.049[‡]
0.1	2.909 (1)	0.0303	0.0021	0.0014	2.942 (10)	2.946[‡]
0.2	2.6810 (5)	0.0379	0.0021	0.0023	2.723 (10)	2.732
0.3	2.4630 (5)	0.0392	0.0017	0.0026	2.516 (10)	2.519
0.4	2.259 (1)	0.0379	0.0013	0.0028	2.301 (10)	2.320
0.5	2.072 (1)	0.0363	0.0011	0.0027	2.112 (10)	2.133
0.75	1.683 (2)	0.0328	0.0007	0.0024	1.719 (10)	1.745
0.8	1.617 (2)	0.0282	0.0005	0.0018	1.647 (10)	

†The $k = 0$ entries are scattering lengths.

‡These polarized orbital results are slightly different from those given in Temkin-Lamkin (Reference 20) because of the fact that integration there was stopped at $r = 20$.

Table 4

Resumé of Calculation for Singlet δ

k	δ_0	$\Delta\delta_0$	$\Delta^2\delta_0^{(1)}$	$\Delta^2\delta_0^{(2)}$	δ	δ(polarized orbital)
0[†]	7.8 (1)				5.6 (4)	5.7
0.01	3.0640(5)	0.026	−0.008	0.004	3.086 (4)	3.085(1)
0.05	2.759 (1)	0.117	−0.035	0.019	2.86 (2)	2.86
0.1	2.420 (3)	0.187	−0.045	0.030	2.59 (3)	2.58
0.2	1.895 (2)	0.215	−0.030	0.034	2.11 (5)	2.11
0.3	1.535 (10)	0.189	−0.016	0.030	1.74 (6)	1.75
0.4	1.269 (1)	0.165	−0.009	0.026	1.45 (6)	1.47
0.5	1.066 (2)	0.148	−0.007	0.023	1.23 (6)	1.25
0.75	0.756 (2)	0.131	−0.0025	0.021	0.91 (6)	0.91
0.8	0.728 (2)	0.126[‡]	−0.002	0.020[‡]	0.87[‡] (6)	

†The $k = 0$ entries are scattering lengths.

‡These entries are different from those quoted in a preprint of this material.

singlet case, the estimated error ranged from 10 percent to 40 percent. We feel that the errors allowed for are rather liberal, particularly in the triplet case. For that reason, we have retained more figures than would seem to be justified by the error. The polarized orbital phase shifts (Reference 18) are included as the last column.

DISCUSSION

The implications of the nonadiabatic theory for the various well-known techniques of calculating (s-wave) scattering problems are clear. The exchange approximation, as representative of the zeroth order problem, has a central role and is by no means a bad approximation. The method of polarized orbitals (Reference 18) and to lesser extent the various exchange adiabatic approximations (Reference 19 and 20) are legitimate next order corrections. The application of these conclusions for electron scattering from other atoms is perhaps even more significant, for in those cases it is difficult to do better than the exchange approximation. But since the polarization is expected to act even more classically, the inclusion of an exchange-adiabatic polarization potential would seem eminently worthwhile where the atomic polarizability is non-negligible. The quantitative alteration, in fact, can be much more pronounced than in hydrogen. In oxygen, for example, the polarization potential decreases the cross section of the zero-energy exchange approximation cross section by a factor of 8, and by a factor of 2 at energies of 10 ev (References 19 and 21). Both decreases seem now to be confirmed by experiment (Reference 22 and 23).

There are, however, at least two related problems which it would also be well to put on a rigorous basis, at least in the case of hydrogen. One is the scattering of higher than s-partial waves, and the second is the inelastic scattering.

Concerning the first problem, we feel that physical intuition should be a reasonable guide as to what techniques are best. Thus, for a given incident energy we would expect the phase shifts to get increasingly further from the exchange approximation phase shifts. This is expected to be so because the higher partial waves are concentrated further from the center, where the adiabatic potential becomes increasingly important relative to other effects. Or, to put it another way, for a given incident velocity, the further away a particle orbit, the more adiabatic its motion appears (an observation that is easily verified on passing airplanes).[10] Nevertheless, the solution of this problem by an extension of our nonadiabatic theory is not trivial. This is because the Schrödinger equation reduces to sets of coupled three-dimensional partial differential equations (Reference 9). In addition, at the lowest energies the polarization must be included in the zeroth order approximation in accord with the fact that the effective range formula gets altered in its first term (References 20, 25, and 26).

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[10]The picture may not be as rosy as might be thought. Recent experiments by Neynaber, Marino, Rothe, and Trujillo (Reference 24) on the (e-H) total elastic cross section, if they are correct, would indicate that the triplet p-wave phase shifts are much closer to the exchange approximation results. This heightens the necessity for a rigorous quantitative theory for the higher partial waves.

The second problem is also difficult to handle by our present method. Consider
for example the s-wave part of the (1s-2s) excitation problem. This is a zero orbital
angular momentum equation governed again by Equation 1. The difficulty here is that the
boundary condition (Equation 8) must contain all states that are energetically accessible.
Even the solution of the zeroth equation (Equation 11) is enormously complicated for the
same reason. We are restricted to the statement that present s-wave close-coupling
approximations which include only s-excited states of hydrogen (References 13 and 27) are
again approximations of only the zeroth order problem (Equation 11). Here, however,
it appears that the zeroth order problem is a much more uncertain approximation of the
whole problem.

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Appendix A

Formulas for Integrals Involving Continuum Coulomb Wave Functions

General Discussion

Formulas for integrals involving continuum Coulomb wave functions are given here. The authors would like to acknowledge the guidance of Dr. L. Maximon in performing these integrations. All formulas are obtainable from the very general formulas of Alder et al.[*] The results involve, among others, the various kinds of hypergeometric and Bessel functions. The notation for these are standard aside from minor variations. Definitions may be found in innumerable books; we mention only Morse and Feshbach.[†] Many of the formulas are not manifestly real, nevertheless, they may all be shown to be real. Those matrix elements which should be symmetric with respect to the interchange of initial and final states can be shown to be symmetric. The reality and symmetry are, in fact, closely related.

The continuum Coulomb functions are normalized as follows:

$$u_p(r) = re^{-ipr} F\left(1 + ip^{-1}; 2; 2ipr\right)$$

$$u_0(r) = \lim_{p \to 0} u_p(r) = \sqrt{\frac{r}{2}} J_1\left(\sqrt{8r}\right) ,$$

where $F(a;b;x)$ is the confluent hypergeometric function; $J_n(x)$ is the Bessel function of order n. In practice all integrals involving the zero energy Coulomb wave function $u_0(r)$, denoted by the index I_0, can be derived from the formulas involving a general p, denoted by Ip, by suitable limiting processes. For the purpose of giving the discrete-continuum matrix elements it is convenient to write the discrete wave functions in the form

$$R_{ns}(r) = e^{-r/n} \sum_{j=1}^{n} C_{nj} r^j ,$$

[*]Alder, K., Bohr, A., et al., "Study of Nuclear Structure by Electromagnetic Excitation with Accelerated Ions," Rev. Mod. Phys. 28(4):432-542, October 1956. (See in particular formula II.B.53.)
[†]Morse, P. M., and Feshbach, H., "Methods of Theoretical Physics," New York: McGraw-Hill, 1953, p. 1725

where C_{nj} is the coefficient of r^j in

$$R_{ns}(r) = (n)^{-1/2}(2rn^{-1})e^{-(r/n)} F(-n + 1; 2; 2rn^{-1}) .$$

All $\tan^{-1}$ functions are to be taken between $-\frac{\pi}{2}$ and $+\frac{\pi}{2}$.

Triplet Formulas

$$(ME)_{Ip_1, Ip_2} = \text{Factor I} \times \text{Factor II} , \tag{A1}$$

where

$$\text{Factor I} = \frac{2\lambda \exp\left[\frac{p_1 - p_2}{p_1 p_2}\tan^{-1}\left(\frac{p_1 - p_2}{\lambda}\right) - \frac{p_1 + p_2}{p_1 p_2}\tan^{-1}\left(\frac{p_1 + p_2}{\lambda}\right) + \frac{i(p_2 - p_1)}{2P_1 P_2}\ln\left(\frac{\lambda^2 + (p_1 - p_2)^2}{\lambda^2 + (p_1 + p_2)^2}\right)\right]}{\left[\lambda^2 + (p_1 - p_2)^2\right]\left[\lambda^2 + (p_1 + p_2)^2\right]}$$

$$\text{Factor II} = F\left(-ip_2^{-1}, ip_1^{-1}; 1; x\right) - \frac{2y\left[\lambda + i(p_1 - p_2)\right]}{\lambda^2 + (p_1 - p_2)^2} F\left(1 - ip_2^{-1}, 1 + ip_1^{-1}; 2; x\right)$$

and

$F(a,b;c;x)$ are hypergeometric functions,

$$\lambda = \kappa_{p1} + \kappa_{p2} ,$$

$$x = \frac{4p_1 p_2}{\lambda^2 + (p_1 + p_2)^2} ,$$

$$y = 1 - x .$$

• • • •

$$(ME)_{I0,Ip} = \text{Factor III} \times \text{Factor IV} , \tag{A2}$$

where

$$\text{Factor III} = \frac{2\lambda}{(\lambda^2 + p^2)^2} \exp\left[\frac{-2\lambda}{\lambda^2 + p^2} - \frac{2}{p}\tan^{-1}\frac{p}{\lambda} + \frac{2ip}{\lambda^2 + p^2}\right]$$

$$\text{Factor IV} = F\left(ip^{-1};\ 1;\ \frac{-4ip}{\lambda^2 + p^2}\right)\ \frac{2(\lambda + ip)}{\lambda^2 + p^2}\ F\left(1 + ip^{-1};\ 2;\ \frac{-4ip}{\lambda^2 + p^2}\right)$$

$$\lambda = \kappa_0 + \kappa_p$$

$$\bullet \quad \bullet \quad \bullet \quad \bullet$$

$$(ME)_{I0,I0} = 2\lambda^{-3} e^{-4/\lambda}\left[I_0\left(4\lambda^{-1}\right) - I_1\left(4\lambda^{-1}\right)\right] , \tag{A3}$$

where

$\lambda = 2\kappa_0$ and $I_m(x)$ are the Bessel function of imaginary argument.

$$\bullet \quad \bullet \quad \bullet \quad \bullet$$

$$(ME)_{n,Ip} = \sum_{j=1}^{n} C_{nj}\mathcal{J}_j(\lambda_{np}) , \tag{A4}$$

where

$$\lambda_{np} = \kappa_n + \kappa_p + n^{-1} ,$$

$$\mathcal{J}_j(\lambda) = \int_0^\infty e^{-\lambda r} r^j u_p(r)\,dr .$$

Hence,

$$\mathcal{J}_j(\lambda) = -\frac{\partial}{\partial\lambda}\mathcal{J}_{j-1}(\lambda) .$$

$$\mathcal{J}_0(\lambda) = \left(\lambda^2 + p^2\right)^{-1}\exp\left[-2p^{-1}\tan^{-1}(p/\lambda)\right] .$$

$$\bullet \quad \bullet \quad \bullet \quad \bullet$$

$$(ME)_{n,I0} \;=\; \lim_{p\to 0} (ME)_{n,Ip}, \tag{A5}$$

and

$$\mathfrak{N}_{s,Ip} \;=\; 2S(\lambda_p)\,\sin\theta$$

$$\mathfrak{N}_{c,Ip} \;=\; 2S(\lambda_p)\,\cos\theta$$

$$\lambda_p \;=\; 1 + \kappa_p$$

$$S(\lambda_p) \;=\; \left(2\lambda p^2\,\sqrt{1+p^2}\right)^{-1}\exp\left(-p^{-1}\tan^{-1}p\right)$$

$$\theta \;=\; \tan^{-1}\!\left(\frac{k}{\kappa_p}\right) + \frac{1}{2p}\,\ln\left[\frac{\lambda_p + p(p-k)}{\lambda_p + p(p+k)}\right]$$

$$\mathfrak{N}_{s,I0} \;=\; \lim_{p\to 0} \mathfrak{N}_{s,Ip}$$

$$\mathfrak{N}_{c,I0} \;=\; \lim_{p\to 0} \mathfrak{N}_{c,I0},$$

where the only non-trivial limit is

$$\theta_0 \;=\; \tan^{-1}\left(\frac{k}{\kappa_0}\right) - k\lambda_0^{-1}$$

Singlet Formulas

The symbols have the same meaning as the corresponding triplet formulas.

$$(SME)_{Ip_1,Ip_2} \;=\; \text{Term V} + \text{Term VI}, \tag{A6}$$

where

$$\text{Term V} \;=\; \left[2\kappa_{p1}\kappa_{p2} + p_2^2 + \kappa_{p2}^2 + \lambda^{-1}\kappa_{p1}\left(\lambda^2 + p_1^2 - p_2^2\right)\right](ME)_{Ip_1,Ip_2}$$

$$\text{Term VI} \;=\; 2\exp\left[\frac{p_1-p_2}{p_1p_2}\tan^{-1}\!\left(\frac{p_1-p_2}{\lambda}\right) - \frac{p_1+p_2}{p_1p_2}\tan^{-1}\!\left(\frac{p_1+p_2}{\lambda}\right)\right.$$

$$\left. + \frac{i(p_2-p_1)}{2p_1p_2}\ln y\right]\frac{F\!\left(1-ip_2^{-1},\,1+ip_1^{-1};\,2;\,x\right)}{\lambda^2 + \left(p_1+p_2\right)^2}$$

$$\bullet \quad \bullet \quad \bullet \quad \bullet$$

$$(SME)_{Ip,I0} = \text{Term VII} + \text{Term VIII,} \qquad (A7)$$

where

$$\text{Term VII} = \left[2\kappa_p\kappa_0 + \kappa_0^2 + \lambda^{-1}\kappa_p(\lambda^2 + p^2)\right](ME)_{Ip,I0}$$

$$\text{Term VIII} = \frac{2}{\lambda^2 + p^2}\exp\left[\frac{2\lambda}{\lambda^2 + p^2} + \frac{2}{p}\tan^{-1}\left(\frac{p}{\lambda}\right) + \frac{2ip}{\lambda^2 + p^2}\right]F\left(1 + ip^{-1};\ 2;\ \frac{-4ip}{\lambda^2 + p^2}\right)$$

$$\bullet \quad \bullet \quad \bullet \quad \bullet$$

$$(SME)_{I0,I0} = \frac{e^{-4/\lambda}}{2\lambda}\left[5I_0\left(\frac{4}{\lambda}\right) - 3I_1\left(\frac{4}{\lambda}\right)\right] \qquad (A8)$$

$$\bullet \quad \bullet \quad \bullet \quad \bullet$$

$$(SME)_{n,Ip} = \text{Term IX} + \text{Term X} \qquad (A9)$$

where

$$\text{Term IX} = \left(\kappa_n - n^{-1}\right)\sum_{j=1}^{n}C_{nj}\left[\left(\kappa_n + \lambda_{np}\right)\mathcal{J}_j(\lambda_{np}) - i\mathcal{J}_{j-1}(\lambda_{np})\right]$$

$$\text{Term X} = \sum_{j=1}^{n}C_{nj}\left[j\left(\kappa_n + \lambda_{np}\right)\mathcal{J}_{j-1}(\lambda_{np}) - (j-1)\mathcal{J}_{j-2}(\lambda_{np})\right]$$

$$\bullet \quad \bullet \quad \bullet \quad \bullet$$

$$(SME)_{n,I0} = \lim_{p\to0}(SME)_{n,Ip}\,. \qquad (A10)$$

$$\bullet \quad \bullet \quad \bullet \quad \bullet$$

and

$$\mu_{Ip} = N_{srIp} - N_{sIp} + kN_{crIp}$$

$$\nu_{Ip} = N_{crIp} - N_{cIp} - kN_{srIp}$$

where

$$N_{srIp} = 2S(\lambda_p)\left[\kappa_n\sin\theta - k\cos\theta\right]$$

$$N_{sIp} = 2\left(\kappa_n + 1\right) S\left(\lambda_p\right) \left[\left(2\kappa_n + 1\right) \sin\theta - k\cos\theta\right]$$

$$N_{crIp} = 2S\left(\lambda_p\right) \left[\kappa_n \cos\theta + k\sin\theta\right]$$

$$N_{cIp} = 2S\left(\lambda_p\right)\left(1 + \kappa_n\right)\left[\left(2\kappa_n + 1\right)\cos\theta + k\sin\theta\right]$$

$$\bullet \quad \bullet \quad \bullet \quad \bullet$$

$$\mu_{I0} = \lim_{p \to 0} \mu_{Ip}$$

$$\nu_{I0} = \lim_{p \to 0} \nu_{Ip} \quad .$$

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is shown to be a variational approximation of the zeroth order problem. A perturbation theory is introduced to calculate the higher order corrections. The dipole correction has an increasingly important quantitative effect in the limit of zero energy. The effect of the long-range part of this correction on the scattering length can be expressed by a formula in terms of inverse powers of a long-range parameter R. Phase shifts are calculated for both singlet and triplet scattering, including up to quadrupole terms. The convergence is such that this number of terms should yield better than four-place accuracy. Uncertainties in the calculated values decrease the accuracy to approximately three significant figures.

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